

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
28 June 2001 (28.06.2001)

PCT

(10) International Publication Number
WO 01/46683 A2

- (51) International Patent Classification⁷: G01N 27/26 Knebelstrasse 16, 98693 Ilmenau (DE). KATHE, Ulrich;
Am Hang 9c, 98693 Ilmenau (DE).
- (21) International Application Number: PCT/EP00/12940
- (22) International Filing Date: 19 December 2000 (19.12.2000) (74) Agents: NIESTROY, Manfred; Geyer, Fehners & Partner
(GbR), Sellierstrasse 1, 07745 Jena et al. (DE).
- (25) Filing Language: English (81) Designated States (national): CN, JP.
- (26) Publication Language: English (84) Designated States (regional): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).
- (30) Priority Data: 09/468,011 20 December 1999 (20.12.1999) US
Published:
— Without international search report and to be republished
upon receipt of that report.
- (71) Applicant: IDC GERÄTEENTWICKLUNGSGE-
SELLSCHAFT MBH [DE/DE]; In den Folgen 5, 98704
Langewiesen (DE).
- (72) Inventors: HERNANDEZ, Herbert, A.; 20202 Post Oak
Hill Drive, Spring, TX 77388 (US). LENK, Norbert, W.;

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TOTAL NITROGEN, SULFUR AND CHLORINE ANALYSIS

(57) Abstract: For analysis of total nitrogen, sulfur and/or chlorine, a solid, liquid or gas sample is combusted with oxygen in a high-temperature furnace to form a combustion gas which is then dried. Dry combustion gas is passed through an electrochemical detector for each element to be measured, the detectors being arranged either in parallel or in series with either arrangement providing an individual determination of the content of the element in the sample. A control system provides a user interface for manipulating and controlling the introduction of the sample to the furnace and the operation of the furnace, dryer and electrochemical detector, and the system stores, records and displays data.

WO 01/46683 A2

5

10 **Title**

TOTAL NITROGEN, SULFUR AND CHLORINE ANALYSIS

FIELD OF THE INVENTION

15 The present invention relates to an apparatus and method for determination of total nitrogen, sulfur and/or chlorine content in aqueous and hydrocarbon matrices, and more particularly to oxidizing a sample by combustion and detecting specific chemical compounds using an electrochemical detector.

20

DESCRIPTION OF THE RELATED ART

In the field of workplace or ambient air monitoring, toxic gas monitors are available for measuring parts per million levels of gaseous nitric oxide (NO), sulfur dioxide (SO₂) and hydrogen chloride (HCl) using electrochemical principles. A worker at risk
25 to exposure to a toxic gas may wear a device for sampling and testing the air he or she breathes. The device may warn the worker of an acute exposure or record a cumulative exposure. Such a device is typically measuring a very minute concentration using a very large sample volume, yet the device must be small enough to be worn by a worker.

30

For example, City Technology, Ltd. of Portsmouth, Hants, England supplies sensors for monitoring contaminants such as NO, SO₂ and HCl in air. City Technology, Ltd. uses an electrochemical detector as its sensor for measuring an air contaminant. A simple sensor operating on electrochemical principles has two electrodes, a sensing
35 electrode and a counter electrode, separated by a thin layer of electrolyte and connected by a low resistance external circuit. Gas diffusing into the sensor is reacted

at the surface of the sensing electrode, by oxidation or reduction, causing a current to flow between the electrodes through the external circuit. The current is proportional to the concentration of gas and can be measured across a load resistor in the external circuit. For reaction to take place the sensing electrode potential must be within a specific range. U.S. Patent Nos. 4,474,648 and 4,587,003, both issued to Tantram et al. and entitled "Gas Sensor," are illustrative of electrochemical gas sensors and are incorporated by reference for all purposes.

As the gas concentration increases so does the current flow, causing a change in the potential of the counter electrode (polarization). With the electrodes connected together by a simple load resistor, the sensing electrode potential follows that of the counter electrode. If the gas concentration continues to rise, the sensing electrode potential will eventually move outside its permitted range. At this point the sensor becomes nonlinear, which effectively limits the upper concentration of gas a two-electrode sensor can be used to measure. Nonlinearity due to polarization is avoided by adding a third electrode, a reference electrode, and using an external potentiostatic operating circuit.

If no reactant gas is present, the sensing electrode will exhibit a small signal, which is known as its baseline. By calibration the baseline can be set to zero, but the magnitude of the baseline increases exponentially with temperature. A fourth electrode, an auxiliary electrode, can be used to offset the effects of temperature changes. Thus, for monitoring workplace or ambient air for contaminants, an electrochemical detector with three or four electrodes is compact, lightweight and sufficiently accurate and reliable, yet it is cost effective.

In the field of industrial process measurements, particularly in refinery and chemical stream and waste analysis, one type of analyzer employed frequently for measuring sulfur and nitrogen content incorporates fluorescent and chemiluminescent detectors, respectively. For example, in U.S. Patent No. 5,152,963 dated October 6, 1992, which is incorporated by reference for all purposes, a total sulfur analyzer system is set forth that operates on gas, liquid or solid samples including free sulfur and sulfur and nitrogen compounds. The sample is first combusted to provide products of combustion including sulfur dioxide (SO_2) and nitric oxide (NO). The SO_2 quantity is measured by exposure to a particular frequency of ultraviolet light to obtain fluorescence, and fluorescent photons are measured by a photomultiplier tube. The NO

is reacted with ozone to form NO_2 , and in this reaction chemiluminescent light is emitted and measured.

5 An analyzer using fluorescence and chemiluminescent detectors requires a number of components such as an ultraviolet light source and associated optics, photomultiplier tubes and an ozone generator. These various components are each a potential source of error in a measurement, and some components are sensitive, delicate or fragile as well as expensive. Consequently, a need remains for a simpler and less expensive laboratory or field analyzer capable of measuring total nitrogen, sulfur
10 and/or chlorine.

SUMMARY OF THE INVENTION

The present invention provides an analyzer system and a method for measuring
15 total nitrogen, sulfur and/or chlorine in a solid, liquid or gaseous sample. The sample is fed to a furnace module where it is burned in the presence of oxygen to produce a combustion gas. Essentially all nitrogen in the sample, except diatomic nitrogen (N_2), is converted to nitric oxide (NO). Essentially all sulfur in the sample is converted to sulfur dioxide (SO_2), and essentially all chlorine in the sample is converted
20 to hydrogen chloride (HCl). Water is typically in the combustion gas and is preferably removed in a dryer. Dry combustion gas is fed to an electrochemical detector, one detector for each specific compound to be measured. A control system provides a user interface for monitoring and controlling several components such as the furnace module and the detector.

25

BRIEF DESCRIPTION OF THE DRAWINGS

A better understanding of the present invention can be obtained when the following detailed description of various embodiments of the invention is considered in conjunction with the drawings, which are described as follows.
30

- Fig.1 is a schematic diagram of an analytical system according to the present invention.
- Fig.2 is a schematic diagram of a control and interface system for the analytical
35 system of Fig.1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to Fig. 1, an analytical system 10 for measuring total nitrogen, sulfur and/or chlorine in a sample is illustrated schematically according to the present invention. An inert carrier gas 12, such as high-purity argon, is fed to a sample introduction apparatus 14, and a mass flow controller 16 regulates the flow of carrier gas 12. Sample introduction apparatus 14 receives the sample for analysis, and the sample can be an aqueous or a hydrocarbon matrix and can be solid, liquid, gaseous or otherwise. Solid samples can be introduced by a quartz capsule or a quartz sample boat. Liquid samples can be introduced by microliter syringe, quartz capsule or quartz sample boat and gaseous samples can be introduced by a gas sample valve or by a gas-tight syringe. The sample introduction apparatus must be suitable for the state of the sample and must be capable of delivering the sample accurately and repeatably.

Oxygen 18, which is preferably a high-purity oxygen, is mixed with the sample from sample introduction apparatus 14, and the mixture is fed to a high-temperature furnace module 20. Oxygen 18 is also fed directly to furnace module 20, and a mass flow controller 22 regulates the combined total flow of oxygen 18. Furnace module 22 includes a high-temperature tube furnace, which can be a quartz combustion tube capable of continuous operation in the range of about 900 to 1200°C or a ceramic combustion tube capable of continuous operation up to at least about 1600°C and preferably up to about 1800°C. The quartz combustion tube is packed with quartz chips, and a type K thermocouple or its equivalent is used for temperature measurement. A cooling fan is provided for removing excess heat from a housing for furnace module 22. A furnace suitable for use as furnace module 20 is available from APS Technologies, Inc. of Spring, Texas.

In furnace module 22 the sample is vaporized in the high-temperature oxygen-rich atmosphere, and the sample is oxidized. This oxidation of the sample and all of its constituents produces a combustion gas containing stable oxides, except for chlorine, which is unstable as an oxide. Chlorine reacts with water in the combustion gas to produce hydrogen chloride (hereinafter referred to as "HCl"), the water being produced as a by-product of combustion or introduced as part of the sample. Thus, chlorine in the sample is converted to HCl. Nitrogen in the sample, except diatomic nitrogen, N_2 , is converted to nitric oxide (hereinafter referred to as "NO"), and sulfur

in the sample is converted to sulfur dioxide (hereinafter referred to as "SO₂"). Nitrogen, sulfur and chlorine in the sample can exist as essentially any compound, and compounds containing the elements nitrogen, sulfur and chlorine in the sample are converted essentially completely to NO, SO₂ and HCl, respectively. Thus, measurement of these compounds provides a measurement of the total amount of these elements in the sample. For example, in a hydrocarbon matrix the nitrogen and sulfur may be bound to a hydrocarbon molecule, and the chlorine may be present as a chlorinated organic compound.

The combustion gas produced in furnace module 22 is dried in a gas dehydration unit 24 to remove water, producing a water-free or dry combustion gas sample. Water in the combustion gas may have been produced in furnace module 22 as an oxidation by-product or, for example, it may have been part of an aqueous sample. In either case it is preferable to remove the water. Gas dehydration unit 24 includes a permeation dryer such as that sold by Perma Pure, Inc. under the registered trademark Nafion, part number PD-624-12PP-APS or an equivalent dryer. Alternatively, a 98% sulfuric acid scrubber with a heated gas transfer tube can be used to remove water from the combustion gas, thus producing the water-free or dry combustion gas sample.

The dry combustion gas sample from gas dehydration unit 24 is fed to a microelectrochemical detector system 26. Micro-electrochemical detector system 26 includes at least one electrochemical detector and as many as three. In this embodiment three electrochemical detectors are illustrated, an electrochemical NO detector 26a, an electrochemical SO₂ detector 26b and an electrochemical HCl detector 26c. Electrochemical NO detector 26a selectively detects NO, and other compounds or species in the dry combustion gas sample do not interfere with the measurement of NO in the sample. Electrochemical SO₂ detector 26b selectively detects SO₂, and other compounds or species in the dry combustion gas sample do not interfere with the measurement of SO₂ in the sample. Likewise, electrochemical HCl detector 26c selectively detects HCl, and other compounds or species in the dry combustion gas sample do not interfere with the measurement of HCl in the sample.

Suitable electrochemical detectors can be obtained from City Technology, Ltd. of Portsmouth, Hants, England. City Technology, Ltd. has a part number 3MNT or equivalent three or four electrode models suitable for use as electrochemical NO

detector 26a, part number 3MST/F or equivalent three or four electrode models suitable for use as electrochemical SO₂ detector 26b, as well as one for electrochemical HCl detector 26c. Electrochemical detector system 26 has solenoid valves 28 for directing sample flow through electrochemical detectors 26a, 26b and 26c, which may be operated in parallel or in series, and if in series, then in any sequence since there is no interference in measurements. Vents 30 are provided for venting the sample from electrochemical detectors 26a, 26b and 26c. All of the electrochemical detectors 26a, 26b and 26c can be used in electrochemical detector system 26 or any one or two can be used. A particular application will dictate which of electrochemical detectors 26a, 26b and/or 26c to use. For more information on electrochemical detectors 26a, 26b and 26c, see the patents concerning electrochemical detectors which were incorporated by reference above.

A control system 32 provides a user interface, processing capability and electronics for operating, through an electronic interface 34, sample introduction apparatus 14, mass flow controllers 16, 22, furnace module 20, gas dehydration unit 24 and electrochemical detector system 26. Dark, heavy lines indicate electrical connection between components, while light, fine lines indicate the flow of sample, carrier gas 12 and/or oxygen 18. Control system 32 uses presently a personal computer, and a graphical interface is provided using software such as that provided by Microsoft corporation under the trademarks Windows 95 or Windows NT. A monitor 36, a keyboard and a pointing device, such as a mouse, provide an interface to control system 32 for a user. Control system 32 stores and displays data via monitor 36 or a printer 38, and control system 32 can be networked with other computers via a network system 40. Software, such as is used typically with such analyzer systems, is provided for control of the various components and for Manipulation, display and analysis of data.

With reference to Fig. 2, more detail is provided for control system 32 and electronic interface 34. Control system 32 includes a PC bus 42, which is the main bus in the personal computer. Four PC boards 44a, 44b, 44c and 44d plug directly into PC bus 42 and provide essentially realtime control for the various components in analytical system 10 while the personal computer provides supervisory control, monitoring and data storage and analysis. PC board 44a is connected to a furnace PC board 46 and is always included. PC board 44a provides essentially realtime control for furnace module 22, sample introduction apparatus 14 and mass flow controllers 16

and 22, as well as for various timed events. At least one of PC boards 44b, 44c or 44d is included, depending on the application and thus the chemical compound to be detected and measured. A detector interface board 48 provides a power, a ground and a signal connection between PC boards 44b, 44c and/or 44d and electrochemical detector cells 26a', 26b' and/or 26c' via coaxial cables. An interconnect cable connects PC board 44a to furnace PC board 46 and PC boards 44b, 44c and 44d to detector interface board 48.

To operate analytical system 10, control system 32 is activated and furnace module 20 is heated to its operating temperature. Inert carrier gas 12, such as dry argon or helium with a minimum purity of 99.9%, and oxygen 18, with preferably a minimum purity of 99.7%, are available from pressurized sources and mass flow controllers 16 and 22, respectively, control flow of these gases through the system. Analytical system 10 is previously assembled with a proper array of electrochemical detectors 26a, 26b and/or 26c for the sample to be analyzed. Depending on the concentration and matrix, a 1 to 100 μL sample is fed to analytical system 10 via sample introduction apparatus 14 using a quartz boat, quartz capsule, syringe or valve as described above. For multiple samples, an automatic sampler can be used for feeding samples sequentially to the system.

Oxygen present in the high-temperature (900 to 1600°C, typically about 1000°C) tube furnace provides a highly oxidative atmosphere for oxidizing the sample as it is carried through furnace module 20. If the sample contains nitrogen, sulfur and chlorine compounds, then combustion gas from furnace module 20 or gas dehydration unit 24 contains NO, SO₂ and HCl, respectively. The sample can contain all three, any one, or any two compounds containing nitrogen, sulfur and/or chlorine. Electrochemical detectors 26a, 26b and/or 26c yield a signal proportional to the concentration of NO, SO₂ and/or HCl, respectively, in the sample, which, by calculation, is used to determine the total nitrogen, sulfur and/or chlorine in the sample. Such determination can be viewed on monitor 36, printed on printer 38 or transferred to another computer via network 40.

Chemiluminescent and fluorescent detectors became the standard or typical detector of choice for measuring total nitrogen and sulfur, respectively. This was the case in spite of the complexity of the equipment due to the number of components and the sensitivity or fragility of the components. In years past alternative detectors

were considered including detectors based on electrochemical analysis. However, electrochemical analysis was dismissed as an unsatisfactory solution, and this view continued to exist until subsequent experimentation resulted in the present invention. Consider the data in Table 1, which is representative data obtained for the analysis of nitrogen in a hydrocarbon matrix by combustion/chemiluminescence and by combustion/electrochemical detection.

TABLE 1.

DETECTOR	Chemiluminescent	Electrochemical
PARAMETER	Nitrogen	Nitrogen
CONCENTRATION, mg/L	5.0	5.0
INTEGRATOR COUNTS	109,658	153,463
STANDARD DEVIATION		
(counts)	7,519	4,517

The electrochemical detector had a higher sensitivity (153,463 vs. 109,658 counts) for measuring nitrogen in the sample than did the chemiluminescent detector. This was a surprising result because in earlier years electrochemical analysis had been dismissed as an unsatisfactory method for determining total nitrogen in a sample. Further, the electrochemical detector had a better repeatability (as indicated by the standard deviation of 4,517 vs. 7,519 counts) than did the chemiluminescent detector. This was also an unexpected result. It was discovered that the signal-to-noise ratio for analytical system 10 is significantly better than that for a prior art system using chemiluminescent and fluorescent detectors, both the sensitivity being greater and the noise being less. A signal-to-noise ratio for a prior art system using chemiluminescent and fluorescent detectors is commonly accepted as 2 to 1, but the signal-to-noise ratio for analytical system 10 is significantly better at 10 to 1 or greater. The detectable quantity of nitrogen, sulfur or chlorine in a sample using analytical system 10 is less than about 1 part per million by weight or 1 mg/kg.

Additional data is provided in Table 2, which is representative data for the analysis of nitrogen, sulfur and chlorine in a hydrocarbon matrix by combustion/electrochemical detection. All samples were injected with a microliter syringe, attached to a liquid autosampler system which tends to remove sampling as a source of error.

TABLE 2.

PARAMETER	Nitrogen	Sulfur	Chlorine
SAMPLE SIZE (μ L)	10	10	10
5 CONCENTRA- TION (mg/L)	1.0	1.0	1.0
INTEGRATOR COUNTS	43,686	23,782	25,911
STANDARD 10 DEVIATION (counts)	± 392	± 688	± 437

The integrator count data in Table 2 indicates good sensitivity for nitrogen, sulfur or chlorine by the electrochemical detectors, and the standard deviation indicates good repeatability.

Thus, it was discovered that electrochemical detectors, which were used for personnel safety monitoring, were better detectors for use in analyzers in the field of industrial process measurements than chemiluminescent and fluorescent detectors. Analytical system 10 and its electrochemical detector system 26 are simpler for a user to operate and maintain than is an analytical system using chemiluminescent and fluorescent detectors. Prior art analytical systems using chemiluminescent and fluorescent detectors require an ozone generator, an ultraviolet light source, optics and photomultiplier tubes, each of which is a source of error, such as baseline drift, and each of which contributes to the cost of building the analytical system.

Analytical system 10 on the other hand requires fewer components, and electrochemical detector system 26 is more durable and capable of withstanding environmental factors encountered typically in a laboratory or field environment. Analytical system 10 is sufficiently durable for use in a field environment as a process analyzer with the addition of a proper housing and enclosure to meet field safety requirements and necessary modifications such as cabling for remote operation. Electrochemical detectors 26a, 26b and 26c are less expensive than some of the components in the prior art analytical system, so analytical system 10 costs less to build than does the prior art system. Analytical system 10 offers the further advantage of chlorine analysis, which is not available in a typical prior art analyzer system used for total nitrogen and/or sulfur analysis.

The foregoing disclosure and description of the invention are illustrative and explanatory thereof, and various modifications and alterations to the embodiments disclosed herein will be apparent to those skilled in the art in view of this disclosure.

5 It is intended that all such variations and modifications fall within the spirit and scope of this invention as claimed.

CLAIMS

5 What is claimed is:

1. An analytical system for measuring total nitrogen and/or total sulfur and/or
total chlorine, comprising:
a furnace system for receiving and oxidizing a sample, the furnace system
10 having an inlet and an outlet and producing a combustion gas stream;
a sample introduction apparatus for delivering the sample to the inlet of the
furnace system; and
an electrochemical detector receiving the combustion gas stream for selec-
tively detecting compounds.
15
2. The analytical system of claim 1, further comprising an electronic control sys-
tem interfaced to the furnace system and the detector for manipulating and
regulating analytical parameters.
- 20 3. The analytical system of claim 1, wherein the furnace system includes a
quartz combustion tube operable up to at least 1200°C.
4. The analytical system of claim 3, wherein the quartz combustion tube is
packed with quartz chips.
25
5. The analytical system of claim 1, wherein the furnace system includes a ce-
ramic combustion tube operable above 1200°C.
6. The analytical system of claim 1, wherein oxygen is used in the furnace sys-
30 tem to oxidize the sample.
7. The analytical system of claim 2, wherein the furnace system includes an elec-
tronic mass flow controller interfaced to the control system.

8. The analytical system of claim 1, wherein the sample introduction apparatus includes a quartz capsule for delivering a solid sample to the inlet of the furnace system.
- 5 9. The analytical system of claim 1, wherein the sample introduction apparatus includes a quartz sample boat for delivering the sample to the inlet of the furnace system.
- 10 10. The analytical system of claim 1, wherein the sample introduction apparatus includes a syringe for delivering the sample to the inlet of the furnace system.
- 15 11. The analytical system of claim 1, wherein the sample introduction apparatus includes a gas sample valve for delivering the sample to the inlet of the furnace system.
- 20 12. The analytical system of claim 1, wherein the detector has at least three electrodes.
13. The analytical system of claim 1, wherein the detector detects nitric oxide (NO).
- 25 14. The analytical system of claim 1, wherein the detector detects sulfur dioxide (SO₂).
15. The analytical system of claim 1, wherein the detector detects hydrogen chloride (HCl).
- 30 16. The analytical system of claim 2, wherein the control system includes a graphical interface for an user, and the control system accumulates and stores data.
17. The analytical system of claim 16, wherein the control system comprises a personal computer system.
- 35 18. The analytical system of claim 17, wherein the furnace system includes a furnace control module and the detector includes a detector control module, and

wherein the control system includes interface boards for interfacing the personal computer system to the furnace control module and to the detector control module.

- 5 19. The analytical system of claim 1, further comprising an enclosure for the furnace system, wherein the enclosure makes the furnace system suitable for use in a field analyzer.
- 10 20. The analytical system of claim 1, further comprising a gas dehydration unit connected to the outlet of the furnace system for removing water from the combustion gas stream.
- 15 21. The analytical system of claim 20, wherein the gas dehydration unit comprises a permeation dryer.
- 20 22. The analytical system of claim 20, wherein the gas dehydration unit comprises a sulfuric acid dryer.
- 25 23. A method for measuring total nitrogen, sulfur and/or chlorine, comprising:
delivering a sample to a furnace system;
oxidizing the sample in the furnace system to produce a combustion gas; and
detecting a compound in the combustion gas using an electrochemical detector.
- 30 24. The method of claim 23, further comprising controlling the furnace system with an electronic control system.
25. The method of claim 23, further comprising drying the combustion gas before the detection step.



